A Preliminary Study on Mechanical-Electrical Behavior of Graphite Powder-Filled High-Density Polyethylene Composites

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ABSTRACT: Mechanical and electrical responses of graphite powder (GP)-filled high-density polyethylene composites to a uniaxial compression–decompression cycle were studied. Above a compression loading level, a large positive-pressure coefficient effect of resistance was observed, for which a slide mechanism of GP in the matrix is believed to be responsible. In a step-wise compressive loading and loading-holding experiment, the critical compression level was also found, at which the resistance response changed from a time-independent one to a time-dependent, creep-like one. The current-voltage behavior of the composites showed that the GP contact was non-ohmic, regardless of GP contents and pressure levels. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 792–796, 2000

Key words: HDPE/GP composites; mechanical–electrical behavior; positive pressure coefficient effect of resistance

INTRODUCTION

The electrical properties of polymer matrix composites containing conductive fillers have been widely studied. Particularly for semicrystalline polymer (e.g., polyethylene) composites, a strong positive temperature coefficient effect of resistance (PTCR) is often observed.[1–3] In general, the conductivity behavior of these composites can be described by the percolation theory,[1] and the PTCR effect is attributed to the larger volume expansion effect of the polymer matrix. Beside the thermal volume expansion for the PTCR effect, other external fields can also alter the volume fraction and the arrangement of the conductive network in the matrix, also resulting in a change in the overall conductivity of the composites. The external fields can include, for instance, hydrostatic pressure, swelling, or mechanical deformation.[4–7]

This article reports mechanical-electrical responses of graphite powder (GP) filled high-density polyethylene (HDPE) composites with different loading levels to mechanical compression ramp, compression jump, step-wise increase in compression, compression-holding, and compression–decompression cycles. The compressive stress–strain behavior and the overall resistance change were simultaneously monitored. Time dependent current-voltage behavior of the composites was also measured. Because of the larger mechanical compressive loading applied in this experiment above a critical level, a slide mechanism of GP in the matrix is believed to be responsible for the larger positive pressure coefficient effect of resistance.

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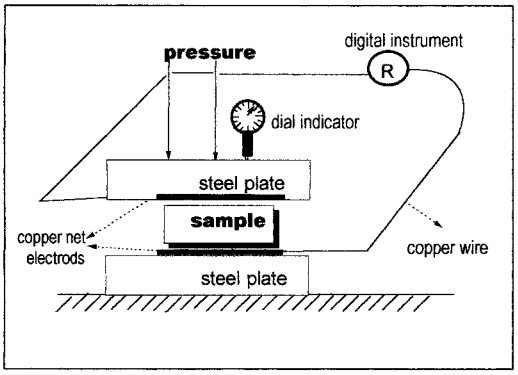

Figure 1 Scheme of resistance measurement under uniaxial pressure.

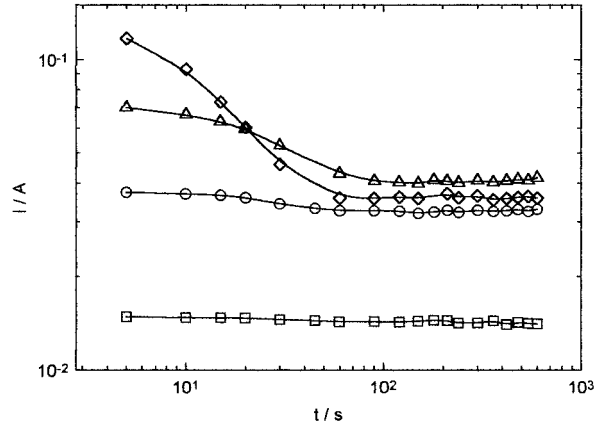

Figure 2 Current–time ($I - t$) plot for 44.4 wt % GP/HDPE composite under different electrical fields of 50 (□), 100 (○), 150 (△), and 200 V cm^{-1} (◇).

EXPERIMENTAL

Colloid graphite (GP) powder with average particle size of 4 μm and purity of 99.85%, and high-density polyethylene (HDPE, 2480) were used. They were mixed on a two-roll mill, and compression molded at 165 ± 5°C/100 kg cm^{-2}/10 min to form plate samples (15 × 15 × 2 mm^3). Two pieces of copper nets were incorporated on the opposite surfaces of the plate as electrodes. No further variation in the sample preparation was done to study these influences.

Two-probe resistance measurement was carried out by using a M890B$^+$ digital Multimeter. An AC electrical field with a constant voltage was applied on the sample, and the effective current was recorded to study the current–voltage ($I - U$) behavior.

The uniaxial compression setup is show in Figure 1. A constant compression speed was maintained to give a strain rate of 0.025 mm min^{-1} for simultaneous stress–strain-resistance measurement. Step-wise loading jump and loading-holding experiments were also performed.

RESULTS AND DISCUSSION

The field dependent current–time ($I - t$) behavior was firstly measured on a 44.4 wt % GP composite sample (Fig. 2). At a low field of 50 V cm^{-1}, I is almost a constant, whereas at higher fields, I decreases with t, due to the voltage-controlled positive resistance effect.[8] This self-heating effect leads finally to an electric-thermal equilibrium current I_e. The beginning current I_0 at $t = 0$ can be used to characterize the initial conductivity of the composite.

Both I_0 and I_e are plotted in Figure 3 against voltage applied, respectively. In the earlier stage, both of them increase linearly, and the curve level corresponds to the loading level of GP. The latter seems to be natural by taking the GP wt %-dependent resistance into the consideration (Fig. 4). The earlier linear $I - U$ relation in Figure 3 can be further described by the following equation[9]

$$I_0 = \alpha V^{\beta} \tag{1}$$

where α and β are empirical constants, independent on the applied voltage. α stands for the conductivity, and β for the deviation from Ohm's law. $\beta = 1$ indicates ohmic contact between the conductive filler particles. Non-ohmic behavior ($\beta \neq 1$) is often reported for polymer composites of

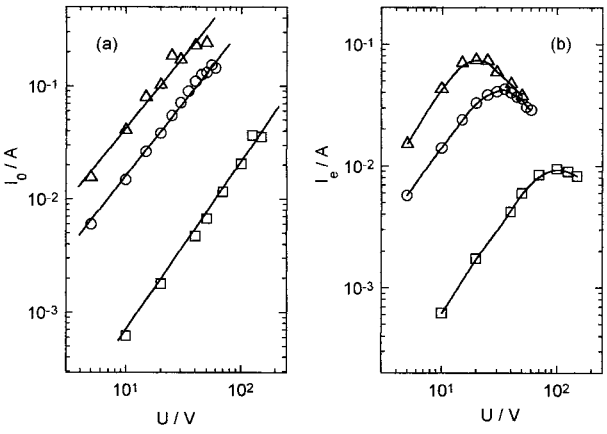

Figure 3 Current-voltage ($I - U$) behavior in the beginning (a) and equilibrium (b) stage for HDPE composites with different GP weight percents of 37.5 (□), 44.4 (○), and 50.0 wt % (△).

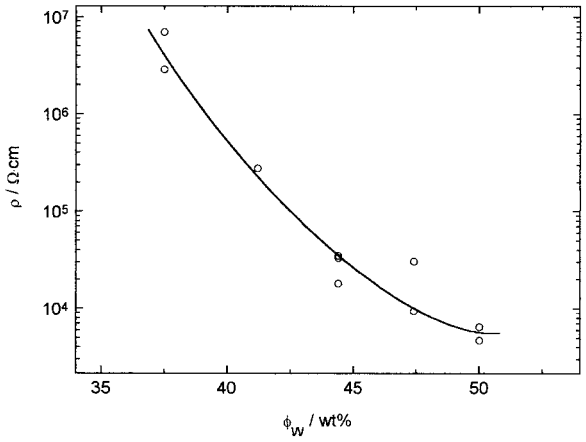

Figure 4 Overall resistivity of HDPE/GP composites against GP weight fraction.

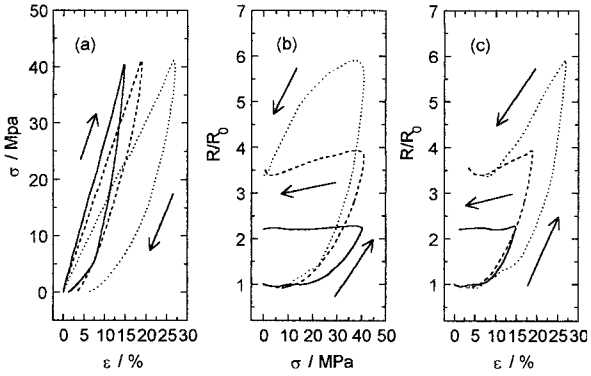

Figure 6 Compressive stress–strain curve (a), and simultaneously measured relative resistance vs. stress (b) and strain (c) for HDPE composites with different GP weight fractions of 50.0 (—), 44.4 (- - -), and 37.5 wt % (· · · · · ·).

second conductivity mechanism due to the presence of dielectric layers in the path of the electrical current.[9] α and β fitted with the data in Figure 3(a) are reported in Figure 5 as functions of GP wt %, indicating a typical non-ohmic behavior. The conductance, R^1, measured before the field applying, agrees well with α.

Under uniaxial compression and decompression cycle, the mechanical and electrical responses of the HDPE/GP composite samples were quite different. Figure 6 shows the simultaneously measured stress–strain-resistance curves for the samples with different GP weight fractions. For the three weight fractions, there is all clearly a linear compressive loading behavior found, followed by a curved unloading (decompression) response. The residual strain is about 2.5% for the GP wt % of 44.4%, indicating a plastic deformation. Lower GP loading results in a relatively smaller residual deformation.

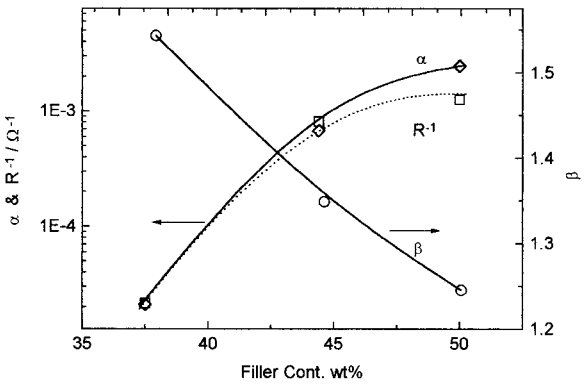

Figure 5 Parameter α and β calculated based on the data in Figure 3 (a) and according to Eq. (1), and measured conductance R^{-1} in dependence on GP weight fraction.

However, the relative overall resistance all rises with the compression after an initial "adjustment," but differently falls down with the decompression, depending on the GP level. The lower the GP level, the higher the change in relative resistance. The initial resistance fluctuation in the compression range of about $\sigma \approx 5$–8 MPa and $\varepsilon \approx 4$–6% might be caused by a better surface contacting, and/or by compacting adjustment of the GP inside the composite. It is noteworthy that there are no resistance dips made by the compression apparent in all the experiments as it is simply expected.

In this article, the pressure dependent resistance is defined, in analog to PTCR effect, as negative and positive pressure coefficient of resistance, NPCR and PPCR, respectively. The NPCR effect was found as a result of hydrostatic pressure, or uniaxial compression in composites, for example, PE/CB,[7] epoxy/Fe_3O_4,[4] and CB-filled conductive vulcanite.[5] It was interpreted on the base of the percolation effect caused by reduction of the volume of insulation phases under pressure,[4,7] or the formation of new conducting networks.[5] PPCR was found in very weakly filled polyurethane/GP composites with a resistivity of about 10^{12} Ω cm. It was attributed to an ionic conduction process due to the hydrostatic pressure.[10] Unlike these composites, however, the electrical behavior of our composites can neither be simply accounted for the increase in volume fraction of GP phase by uniaxial compression for the NPCR, nor for an ionic conduction process for the PPCR effect. It is evident that the larger mechanical deformation, particularly the transverse deformation of the whole sample in the

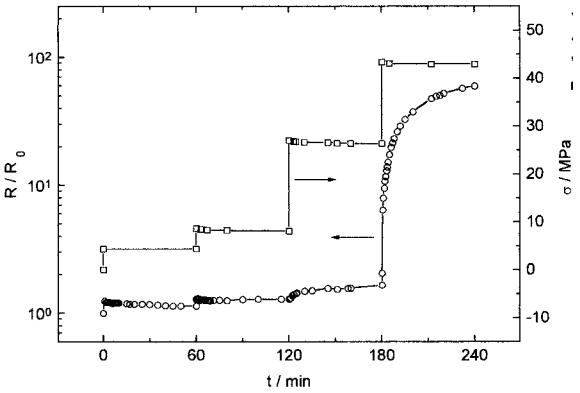

Figure 7 Step-wise compressive loading and loading–holding curve, and the simultaneously measured relative resistance response for 44.4 wt % GP/HDPE composite.

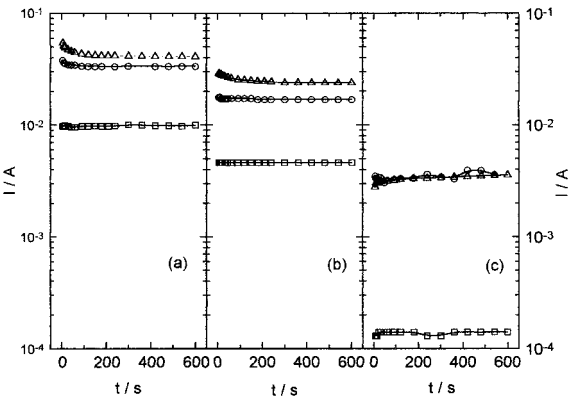

Figure 8 Effect of uniaxial pressure of 7.8 (a), 26.0 (b), and 42.4 MPa (c), and electrical field of 200 (□), 600 (○), and 1000 V cm^{-1} (△) on the $I - t$ curves for 44.4 wt % GP/HDPE composite.

range of $\varepsilon \approx 4$–7%, is responsible for the large PPCR effect.

The loading and unloading curves do not coincide (Fig. 6), and there exists a large residual resistance increase at the end of the mechanical cycle, with the amount of GP increasing, suggesting an irreversible slide mechanism of GP. The layered structure of GP leads obviously to slide layer by layer in GP,[11,12] and subsequently to breakdown of the conductive contact across the medium. For both the GP loading of 37.5 and 44.4%, the relative residual resistance is about 3.5. And for GP of 50.0%, it is about 2.2.

The resistance response to a compression jump can be "elastic," i.e., time independent, or time dependent. This is demonstrated in Figure 7. For the first two jumps up to a compression level of about 8 MPa, it immediately follows an increase in resistance, and then it levels slightly off. However, for the next two jumps from 8 MPa up to 26.5 MPa and 43.5 MPa, respectively, a time-dependent, creep-like response in R/R_0 takes place. At each end of the first three jumps, a respective resistance level is reached, which is comparable with that corresponding to the continuous compression ramp in Figure 6. This behavior suggests that: (1) there is a transition limit at the third jump that determines whether the resistance response is time dependent or not to the compression jump, and (2) time is needed to rearrange the conductive structure inside the composite for loadings higher than that critical level.

Comparing the mechanical-electrical response to the step-wise compression jump with that to the compression ramp, it is obvious that the first two time-independent jumps lie just in the phase of the resistance "adjustment" discussed previously. In this compression range, the slide mechanism of GP might not work. Only if the compression exceeds this level, the layered GP structure begins to slide, leading to a time-dependent resistance increase.

Also due to the resistance increase caused by the compression, a different behavior comes into the existence in time-dependent current measured after a 1-h compression holding. This is clearly demonstrated in Figure 8 by comparing the $I - t$ behaviors in Figures 2 and 8 for the 44.4 wt % GP/PE composites. The higher the pressure, the higher the resistance, and thus the lower the current because the self-heating effect is almost eliminated by the higher resistance and the less the time dependence of the current. The compression-induced resistance increase affects also the I

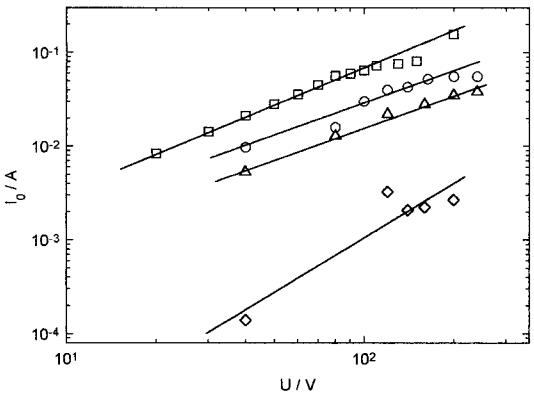

Figure 9 $I - U$ behavior of 44.4 wt % GP/HDPE composite under uniaxial pressure of 0 (□), 7.8 (○), 26.0 (△), and 42.4 MPa (◇).

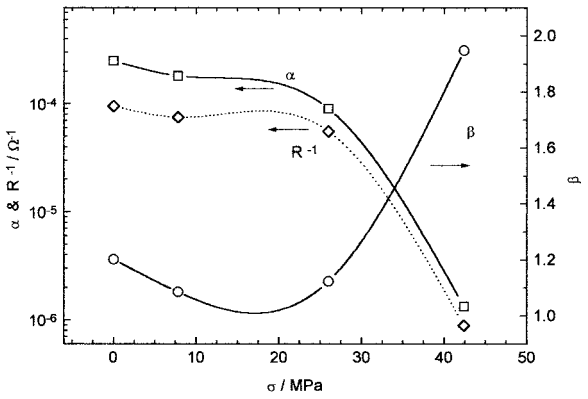

Figure 10 Effect of uniaxial pressure on the parameters α, β, and R^{-1}.

$-$ U behavior in such a manner that the $I - U$ curves fall with the pressure (Fig. 9), and there is still a non-ohmic but high-resistive contact in the composite. This change is shown in Figure 10 in the parameter α and β, respectively. Further study should quantitatively explore the relationship between the mechanical deformation and the resistance behavior.

CONCLUSION

Mechanical and electrical responses to compression–decompression cycles were studied on GP loaded HDPE composites. As the composite was largely compressed, the resistance rose after an initial surface adjustment, indicating a large PPCR effect. It is believed that the slide mechanism of the GP in the matrix is responsible for the PPCR effect. By a step-wise loading and loading holding, it came to a time-independent resistance increase below and a time-dependent creep-like one above a critical compression. The time-independent resistance behavior took place actually in the compression range of the initial resistance adjustment, while the time-dependent one occurred in the range where the PPCR effect appeared. In all the experiments, the NPCR effect was not observed. The GP contact was non-ohmic, irrespective of the pressure and the GP percent.

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